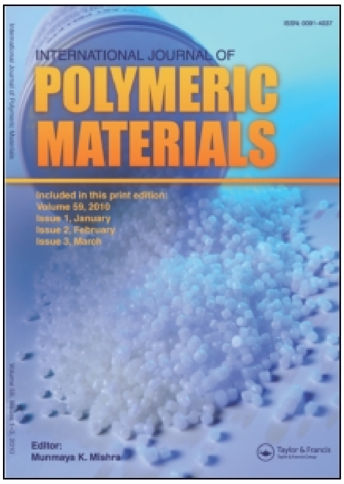

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Some Problems of Structure Formation in Self-Organizing Liquid Oligomer Systems

III. Analysis of Curing of Oligoesteracrylate Blend Systems within the Framework of the Avrami Model*

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The analysis of curing process of oligoesteracrylate blend system is carried out using the Avrami model.

Keywords: Oligoacrylate blend; phase transformation; curing Avrami model

INTRODUCTION

The information on phase transformations taking place during chemical curing of different types of oligomer systems can be gained using various methods (for example, see the monographs and reviews [1–7]), among them the formalization of kinetic curves "degree of conversion α – time τ" within the framework of the Avrami model approximations. This extremely formal model developed and

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successfully tested for the analysis of crystal growth velocity [8,9] was first applied in [2] for the study of network formation processes and its validity for such purposes was further proved by a number of independent methods [10, 11].

RESULTS AND DISCUSSION

The essence of the analysis of phase transformations in the process of chemical reactions proceeding is as follows. Kinetic curves are replotted in the coordinates

$$\alpha = 1 - \exp(-K\tau^n), \tag{1}$$

where α is the degree of conversion, $K \sim k_g/k_t$ is the specific rate of polymerization proportional to the ratio of the constants of the growth and termination rates, τ is the elapsed time of reaction, n is a coefficient depending on the polymerization conditions. n is taken to be equal to 1 if a reaction takes place in a homogeneous medium (the rate of chemical reaction is much more than the rate of phase separation). If a reaction proceeds as a heterogeneous one (the phase separation rate exceeds the rate of chemical reaction) then $n \rightarrow 3$. All the variations of n within the limits of $1 < n < 3$ reflect a superposition of the homogeneous (inside the body of a solution) and the heterogeneous (in the neighbourhood of the interface) components of a polymerization process. The value of n equal to zero indicates that a reaction has come to a halt.

Thus, from the character of dependencies $n = f(\tau \text{ or } \alpha)$, one can judge the kinetics of phase degradation and the extent of localization of a polymerization process in the neighbourhood of the phase boundary during a chemical reaction in a liquid medium. Related analysis of the kinetics of phase formation during the initiated polymerization of individual OEA's in the presence of a pre-polymerization inhibitor was performed in the papers [12–14]. It is considered below for the reactions of curing of a number of oligoesteracrylate blends.

Trioxyethyleneglycol dimethacrylate and its blends with its saturated analogue – trioxyethyleneglycol diisobutyrate – and also with PVC were chosen as the objects of investigation. The techniques of synthesis and purification of the components are described in [12, 13].

Besides, in this papers the initial kinetic curves of radically initiated polimerization are given for the oligoesteracrylate containing 0.007 w.% of hydroquinone and for its blends, obtained by the IR spectroscopy method from the decrease of intensity of the $C=C$ stretch vibrations band (1635 cm^{-1}).

In Figure 1, the anamorphoses of the kinetic curves are depicted in the coordinates of Eq. (1) for the curing process of initially one-phase mixtures of trioxyethyleneglycol methacrylate with its saturated analogue. In this Figure weight fractions ω_1 of the reactive component are labelled by the figures from 0,1 to 1,0 placed at the edges of the curves; the values of n at different stages of curing are labelled by the figures along the curves. The limits of these stages are shown by the arrows.

One can see that, in complete agreement with the scheme of OEA curing offered by A. A. Berlin [15], the polymerization process starts and proceeds for some time (to the values of $\alpha=\alpha_{cr}$) as a homogeneous one (n = 1). Then at $\alpha \geq \alpha_{cr}$ the value of n begins to rise. At

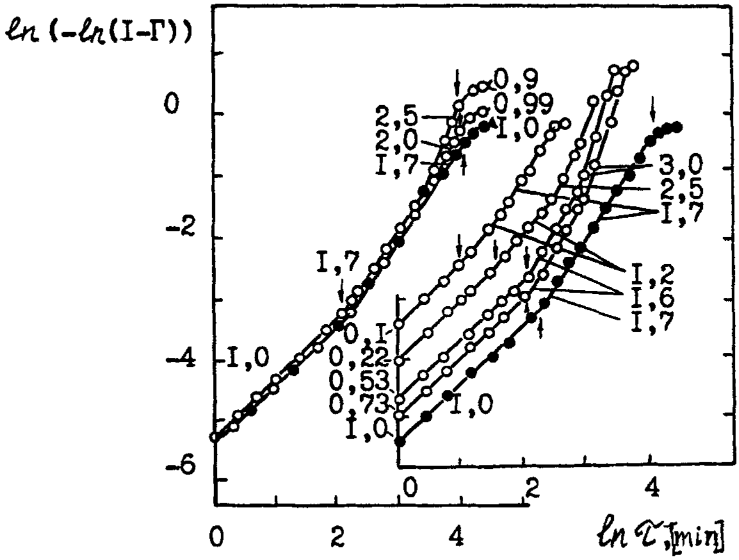

FIGURE 1 The anamorphoses of the kinetic curves of polymerization of trioxyethyleneglycol dimethacrylate in the blend with its saturated analogue in the coordinates of Eq. (1) at T = 110°C (the initiator is 0.5% dicumyl peroxide) in the range of ω_1 = 1,0 – 0,1. The explanation is in the text.

this stage, for the given systems the values of α_{cr} oscillate from 1 to 4% and of n from 1.2 to 1.7 depending on the magnitude of ω_1. It means that at $\alpha \geq \alpha_{cr}$ the chemical reaction begins partially to localize on the surface of particles formed as a result of phase degradation occurred at the corresponding degrees of conversion. As the conversion of double bonds increases n rises up to the values close to 3 and the polymerization progresses as a frontal one. Within such a regime the reaction proceeds up to $\alpha = \alpha_m$, followed by the third step of monolithization resulting in the decrease of the particle surface on which the polymerization process is localized; the values of n decline gradually to zero. In accordance with the scheme of polymerization suggested for high degrees of conversion [6, 16] and with the scheme of polycondensation considered in [17], α_m may be interpreted as a point of phase inversion. For the investigated oligomer blends α_m ranges from 50 to 80% within the chosen curing regimes.

The comparison of the data represented above with the results obtained in [13, 18] allows the conclusion that there is no essential difference in the characters of phase separation in the process of chemical curing of both the basic oligomers and their blends. In both cases the following three "mechanisms" of the process progression take place: a homogeneous one at $\alpha \leq \alpha_{cr}$; the beginning of phase degradation at $\alpha = \alpha_{cr}$ and thus on the interval $\alpha_{cr} < \alpha < \alpha_m$ there are two types of reactions – inside the body of a solution and on the surface; and, finally, at the stages preceeding the monolithization and at $\alpha \geq \alpha_m$ the reactions within the body of a solution are almost completely suppressed. The second component influence appears not only in mixing α_{cr} and α_m values but also in the increase of the extent of polymerization localization in the neighbourhood of the phase boundary. This fact is of fundamental importance since it results in the change of integral values of chemical reactions rates at the subsequent stages and in the change of phase separation rates and in the deviation from the equilibrium level and in the variation of the extent of microsineresis of not reacted molecules from the network and in the change of other structural parameters of a cure system as well. The degree of the medium influence is controlled by the second component dosage, its viscosity, the temperature of the process and so on. Some qualitative manifestations of such dependencies are given below.

For example, if the second component is characterized by a viscosity which approaches to the viscosity of the reactive component then at its low concentrations ($\omega_2 < 10\%$) the kinetics of structure transformations in OBS's at the first stage of the polymerization does not essentially alter comparing with the "block" (one-component) variant of curing. But at the second and at the third stages of the process the presence of an inert diluent is reflected by the acceleration of phase separation and by the increase of the conversion degrees at which the inversion and monolithization begin. The increase of $\omega_2 > 10\%$ (within the limits of one-phase state) affect the kinetics of phase separation at all three stages: α_{cr} and α_m rise proportionally to ω_2, the magnitude of n at the second stage therewith grows, *i.e.*, in this case the contribution of heterogeneous reactions increases and, consequently, the limiting value of conversion degree increases.

The influence of the phase state of the system and of the curing temperature of oligomer blend systems on the kinetics of phase separation is illustrated in Figure 2 which presents the kinetic anamorphoses of curing of the PVC-trioxyethyleneglycol methacrylate blend at various temperatures. The components dosages were chosen so as to overlap the regions of the one-phase state to the left ($\omega_1 = 0.1$ and

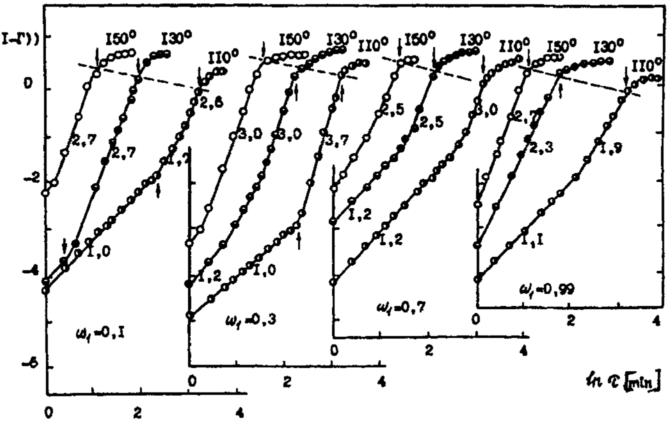

FIGURE 2 The anamorphoses of the kinetic curves of polymerization of trioxyethyleneglycol dimethacrylate in the blend with PVC in the coordinates of Eq. (1) at different T and ω_1. The explanation is in the text.

0.3) and to the right ($\omega_1 = 0.99$) of the binodal and also the region of two-phase state ($\omega_1 = 0.7$).

At the curing temperature of 150°C (≅UCST) which provides extremely high rates of polymerization, the initial phase organization of the oligomer blend is not essential in that at any phase state the process begins at once as a heterogeneous one ($n = 2.5 - 3.0$), *i.e.*, the rigid network forms as a result of the very first acts of polymerization. The homogeneous stage of the process (following Berlin [15] – a β-polymer formation) is not detected under the given conditions (at achievable velocities and at the chosen time of observation).

The differences related to the influence of initial phase state of OBS's on the processes of their phase separation are revealed at curing temperatures T lower than UCST. At 110°–130°C in the solution with an excess of the polymer (a situation to the left of the binodal), where the rates of polymerization are even lower than in the case of homopolymerization [14], the process begins homogeneously (to $\alpha_{cr} = 1-6\%$, the interval is determined by the dependence of α_{cr} on ω_1 and T), without marked phase separation ($n \approx 1$). In contrast, in the solution with an excess of the oligomer (to the right of the binodal) n becomes at once > 1 and the rate of phase separation at the second stage is higher. In this case the reactive oligomer is thickened with the solved polymer [19] and the initial rate of polymerization W_0 is 3–5 times higher than that of individual oligomer curing [20], and clearly even higher than in the solution with the lack of the oligomer. In two-phase systems, which are the mixtures of the solutions mentioned above, the polymerization process starts simultaneously in both coexisting phases, within each of them it proceeding mainly in accordance with the regularities of curing of the corresponding solutions. Therefore the magnitudes of the structural-kinetic parameters registered during the initially two-phase systems curing have the character of averaged values. However, in contrast with the initial rate of polymerization W_0 [20], their averaging does not obey the law of additivity.

Let us note one more essential detail. One of the curves in Figure 2 ($\omega_1 = 0.3$ and $T = 110°$) is characterized by the value of $n > 3$ at the second stage that contradicts the postulates of Avrami model. However, this contadiction is not fundamental. The mentioned fact ($n > 3$) takes place for various reactive systems [12] and has been known since the works of Mandelkern [8] on crystallization. It can be explained very simply [8]: not only the growth of crystals is possible but a sporadic generation of new centers of crystallization in the process as well, that is not taken into account within Avrami model. If this is the case, as applied to polymerization processes, the value of $n > 3$ means the following: if phase formation proceeds *via* the nucleation mechanism then, as the polymerization process progresses, not only the growth of heterophase particles sizes occurs but also new centers of network formation may appear. The theoretical and experimental evidence of this conclusion is presented in the papers [7, 21 – 23].

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